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Description

The present invention relates to an improved process for the selective production of secondary amines from tertiary amines and of primary amines from secondary amines by catalytic oxidation in the presence of an activated carbon catalyst of which the catalytic activity has been enhanced.

U.S. Patent 4,264,776 discloses and claims a process for preparing secondary amines by catalytic oxidation of tertiary amines with oxygen over carbon catalyst. The catalyst is an activated carbon of the type well known in the art and characterized by high absorptive capacity for gases, vapors, and colloidal solids and relatively high specific surface areas. Activation of commercially available carbon catalysts is usually achieved by heating the carbon to high temperatures (800°C to 900°C) with steam or with carbon dioxide which brings about a porous particulate structure and increased specific surface area.

U.S. Patent 4,072,706 discloses a process for oxidative removal of phosphonomethyl groups from tertiary amines in which a molecular oxygen-containing gas is employed along with an activated carbon catalyst. It is noted that any source or form of carbon can be used as a catalyst or substrate in the process of the disclosed invention.

U.S. Patent 3,969,398 teaches the use of activated carbon in the catalytic oxidation of N - (phosphonomethylimino)diacetic acid. It is stated that the carbon catalysts useful in the claimed process are available under a large number of trade names.

U.S. Patent 3,497,564 discloses the use of amorphous or graphitic carbon as a catalyst in the oxidative dehydrogenation of alkylbenzenes. It is taught that activated carbon of whatever origin is operable in the process.

Japanese Patent Application 56-17634 discloses an activation method for SO₃/SO₂ conversion carbon materials which are useful as reduction catalysts to convert selectively SO₃ in various gases, such as air and exhaust, to SO₂. Carbon materials, such as cylindrical activated carbon, are treated with an oxidizing acid, e.g., nitric acid, followed by heat treatment at 300°C to 700°C under an inert gas.

U.S. Patent 4,158,643 teaches a method for oxidative modification of an activated carbon support in which oxygen is added to the surface of the activated carbon, and then the carbon support is impregnated with an inert hydrophobic compound. The carbon support, which may be any commercially available activated carbon for vapor phase activation use, is useful in oxidizing carbon monoxide in the presence of sulfur dioxide for an extended period of time.

U.S. Patent 3,243,383 teaches a method for regenerating spent catalysts which have been used for polymerizing olefins to liquid products. According to the disclosure, spent cobalt oxide on carbon catalyst is heated in an inert atmosphere, cooled, and then treated with nitric acid, nitric oxide, or nitrogen dioxide.

None of the foregoing references suggests that the surface of a carbon catalyst, particularly where acidic and basic surface oxides can be present, can play an important role in amine oxidation rates.

This invention provides an improved process for the selective production of secondary amines and primary amines by bringing together under reaction conditions respectively a tertiary amine or a secondary amine with oxygen or an oxygen-containing gas in the presence of an activated carbon catalyst, wherein the improvement derives from the use of an activated carbon catalyst wherein oxides have been removed from the surface thereof.

In one method of accomplishing the removal of surface oxides, a treatment sequence is followed which comprises subjecting the carbon material to an oxidizing agent, such as nitric acid, CrO₃, H₂O₂, hypochlorite and the like, or an oxidant gas, such as H₂O, H₂O/NH₃, CO₂, NO_x, air, etc. and then pyrolyzing it in an oxygen-free atmosphere at a temperature in the range of about 500°C to 1500°C.

In a second method, the removal is accomplished by simultaneously pyrolyzing the carbon material in the presence of NH₃ and an oxygen-containing gas that will react with the oxides on the surface of the carbon at pyrolyzing temperatures. Suitable oxygen-containing gases include steam, NO_x, O₂, CO₂, SO₂ and mixtures of such gases.

As used herein the term "oxides" is intended to mean carbon functional groups which contain oxygen as well as hetero atom functional groups which contain oxygen. Other hetero atom functional groups which do not contain oxygen may also be removed from the surface of the carbon material during treatment.

Activated carbons prepared for use in the process according to this invention demonstrate unexpectedly improved activity, i.e., reaction rates, in the catalytic oxidation of tertiary amines to selectively produce secondary amines. Moreover, the oxidative removal of carboxymethyl and phosphonomethyl groups from tertiary amines and secondary amines and the catalytic oxidation of N - (phosphonomethylimino)diacetic acid can be significantly enhanced using a carbon catalyst treated according to this invention, without regard to the kind of carbon material employed.

Detailed description of the invention

The activity of carbon used as a catalyst in the oxidation of tertiary amines to secondary amines and in the oxidation of secondary amines to primary amines, according to the present invention can be greatly enhanced if the carbon material is first subjected to a treatment process to remove surface oxides. In carbon catalyzed oxidation reactions, an analysis of the catalysis mechanism tends to suggest a possible correlation between catalyst activity and surface area and/or pore size distribution. It has now been

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discovered that the presence of basic and acidic oxides on the surface of the carbon material can play a significant role in the oxidation process. Although applicant does not wish to be bound by any particular theory, it is believed that the catalytic activity of the catalyst can be substantially increased if the acidic oxides are removed from the surface of the carbon.

5 U.S. Patent 4,264,776, the teachings of which are incorporated herein by reference, describes a wide variety of carbon materials which can be used in practicing this invention. Ordinarily the carbon catalyst is a commercially available activated carbon with a carbon content ranging from about 10% for bone charcoal to about 98% for some wood chars and nearly 100% for activated carbons derived from organic polymers. The noncarbonaceous matter in commercially available carbon materials will normally vary depending on
10 such factors as precursor origin, processing, and activation method. For example, inorganic "ash" components containing aluminum and silicon can be present in large amounts accompanied by certain alkali metals and alkaline earths. The latter grouping influences the acidity-basicity characteristics of the activated carbon. Among other inorganic elements often found in activated carbons are iron and titanium. Depending on raw material origin and activation procedure, large amounts of oxygen can be present along
15 with lesser amounts of hydrogen, nitrogen, sulfur, and other organic functional groups. Despite the wide variety of elements and impurities which can comprise an individual commercially available carbon material, the treatment of the carbon materials for use in the process of this invention is applicable to all commercially available activated carbon catalyst materials.

20 Following is a listing of some of the activated carbons which have demonstrated enhanced activity after treatment for use according to this invention. The list is presented for illustration and should not be interpreted as limiting the applicability of this invention. Preferably, the carbons are in the form of powders, although granules or any other suitable particulate form or shape can be employed in practicing this invention.

25	Trade Name	Sold by
	Darco G-60 spec	ICI-America Wilmington, Delaware
	Darco X	ICI-America Wilmington, Delaware
30	Norit SG extra	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit EN4	Amer. Norit Co., Inc. Jacksonville, Florida
35	Norit EXW	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit A	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit ultra-C	Amer. Norit Co., Inc. Jacksonville, Florida
40	Norit ACX	Amer. Norit Co., Inc. Jacksonville, Florida
	XZ	Barnebey-Cheney Columbus, Ohio
45	NW	Barnebey-Cheney Columbus, Ohio
	JV	Barnebey-Cheney Columbus, Ohio
	BL pulv.	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
50	PWA pulv.	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
55	PCB fines	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
	P-100	No. Amer. Carbon, Inc. Columbus, Ohio
60	Nuchar CN	Westvaco Corporation Carbon Department Covington, Virginia
	Nucher C-1000N	Westvaco Corporation Carbon Department Covington, Virginia

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	Trade name	Sold by
	Nuchar C-190A	Westvaco Corporation Carbon Department Covington, Virginia
5	Nuchar C-115A	Westvaco Corporation Carbon Department Covington, Virginia
	Code 1551	Baker and Adamson division of Allied Amer. Norit Co., Inc. Jacksonville, Florida
10	Norit 4x14 mesh	Amer. Norit Co., Inc. Jacksonville, Florida
	GI-9615	Barnebey-Cheney Columbus, Ohio
15	VG-8408	Barnebey-Cheney Columbus, Ohio
	VG-8590	Barnebey-Cheney Columbus, Ohio
	NB-9377	Barnebey-Cheney Columbus, Ohio
20	Grade 235	Witco Chemical Corp. Activated Carbon Div. New York, New York
	Grade 337	Witco Chemical Corp. Activated Carbon Div. New York, New York
25	Grade 517	Witco Chemical Corp. Activated Carbon Div. New York, New York
	Grade 256	Witco Chemical Corp. Activated Carbon Div. New York, New York
30	Columbia SXAC	Union Carbide New York, New York

In practicing this invention, the treatment of the carbon catalyst can be accomplished by a single or a multi-step scheme which in either case results in an overall chemical reduction of oxides on the carbon surface, i.e., a reduction or removal of acidic oxides from the carbon surface.

In a two-step scheme, the carbon material can be first treated with an oxidizing agent such as, for example, liquid nitric acid, nitrogen dioxide, CrO_3 , air, oxygen, H_2O_2 , hypochlorite, or a mixture of gases obtained by vaporizing nitric acid. The treatment can be accomplished using either a gas or a liquid oxidizing agent. Where a liquid is used, concentrated nitric acid containing from about 10 to about 80 gm HNO_3 per 100 gm of aqueous solution is preferred. Preferred gaseous oxidants include oxygen, nitrogen dioxide, and nitric acid vapors. A particularly effective oxidant is nitric acid in the vapor phase which includes nitric acid carried into the vapor phase by an entraining gas as well as the vapors obtained by distilling liquid nitric acid. With a liquid oxidant, temperatures from about 60°C to about 90°C are appropriate, but with gaseous oxidants, it is often advantageous to use temperatures of about 50°C to about 500°C or even higher for the treatment step.

The treatment can be achieved by placing carbon from a manufacturer in a round bottom flask which contains a magnetic stirring bar. Liquid nitric acid is selected as the oxidizing agent for illustration. The amount of carbon used is determined by the percent carbon load desired (% carbon load=gm of carbon used per 100 ml of nitric acid solution) and the nitric acid solution volume to be used. Ordinarily, 1 to 200 gm of carbon per 100 ml of nitric acid or other liquid oxidizing agent is satisfactory. Temperature control can be provided by any suitable means. A condenser and scrubber can be connected to the round bottom of the flask as desired. A calculated volume of water, preferably deionized water, is added to the carbon, followed by sufficient 69—71% nitric acid to achieve the desired nitric acid solution. The carbon and nitric acid solution are then stirred for the desired period at the desired temperature. Experimental results indicate that carbon load, temperature, nitric acid concentration, etc. in the first treatment step are not particularly critical to achieving the desired oxidation of the carbon material and thus may be governed by convenience over a wide range. The highest possible carbon load is preferred for economic reasons.

After stirring the carbon is filtered, and the resulting wet cake may or may not be washed and/or dried prior to pyrolysis.

The time during which the carbon is treated with the oxidant can vary widely from about 5 minutes to about 10 hours. Preferably, a reaction time of about 30 minutes to about 6 hours is satisfactory. When concentrated nitric acid is the oxidant, a contact time of about 30 minutes to about 3 hours is satisfactory.

In a second step, the oxidized carbon material is pyrolyzed, i.e., heat treated, at a temperature in the range of about 500°C to about 1500°C, preferably from about 800°C to 1200°C. In one embodiment of this

invention, the pyrolysis is conducted in an atmosphere such as nitrogen containing small amounts of steam or carbon dioxide, which is believed to aid in the pyrolysis. As will occur to those skilled in the art in view of this disclosure, the oxides will be removed from the surface of the carbon at pyrolysis temperatures, but the presence of oxygen-containing gases such as steam or carbon dioxide should be avoided as the carbon cools below pyrolysis temperatures to avoid the re-formation of surface oxides. Accordingly, it is preferred to conduct the pyrolysis in an inert gas atmosphere, such as nitrogen, argon or helium.

Wet cake or dry carbon is placed in a ceramic pyrolysis dish which together are placed in a quartz tube. In one embodiment of this invention, nitrogen gas is passed through water at about 70°C, then through the quartz tube during pyrolysis. In an alternate embodiment, a dry, static nitrogen atmosphere is maintained after flushing the quartz tube with several tube volumes of dry nitrogen prior to pyrolysis. The quartz tube containing the pyrolysis dish is placed in a suitable pyrolyzer apparatus at about 930°C for the desired period, followed by cooling while maintaining the nitrogen atmosphere.

Pyrolysis can last anywhere from about 5 minutes to 60 hours, although 10 minutes to 6 hours is normally satisfactory. The shorter times are preferred for economic reasons because, as might be expected continued exposure of the carbon to elevated temperatures for prolonged periods can result in a poor carbon catalyst for the oxidation. In addition, although applicant does not wish to be bound by any particular theory, it is believed that prolonged heating at pyrolysis temperatures favors the formation of graphite, and it is believed that graphite is not as satisfactory as activated carbon for the oxidative conversion of tertiary and secondary amines to secondary and primary amines. It is preferred that the pyrolysis occurs in a slightly moist atmosphere or an atmosphere which contains NH_3 as this appears to produce a more active catalyst in a shorter time.

In a preferred method of treatment to remove surface oxides, the treatment is accomplished in a single step by pyrolyzing the carbon material as described above while simultaneously passing a gas stream comprised of NH_3 and an oxygen-containing gas e.g., $\text{H}_2\text{O}/\text{NH}_3$, through the carbon. Although it is not a critical feature of this invention, the flow rate of the gas stream should be fast enough to achieve adequate contact between fresh gas reactants and the carbon surface, yet slow enough to prevent excess carbon weight loss and material waste. Many NH_3 /oxygen-containing gas mixtures can be used such as, for example, NH_3/CO_2 , NH_3/O_2 , $\text{NH}_3/\text{H}_2\text{O}$ and NH_3/NO_x , provided the gas mixture achieves the desired result. Ordinarily, the oxygen-containing gas/ NH_3 streams contains not more than 90 parts by volume of the oxygen-containing gas per 100 parts by volume of gas stream. Furthermore, nitrogen can be used as a diluent to prevent severe weight loss of the carbon in high oxygen-containing gas concentrations. Ammonia is a basic gas, and, as such, is believed to assist the decomposition of the various oxide groups on the surface of the carbon material. Any other chemical entity which will generate NH_3 during pyrolysis should also prove satisfactory as an NH_3 source. For economic reasons an $\text{NH}_3/\text{H}_2\text{O}$ gas stream is most preferred in practicing the process of this invention.

The treated carbon materials used in the catalytic oxidation of tertiary amines and secondary amines according to the process of this invention, demonstrate substantially increased activity, i.e., faster reaction rates, than commercially available activated carbons. Reaction rates, for example, can be increased up to 30 times and higher the rate obtainable with otherwise untreated commercial activated carbon catalysts, all other oxidation reaction conditions remaining unchanged. Surprisingly, even carbons which are initially inactive, such as carbon black and sugar charcoal, for example, can be activated according to the process of this invention. In addition to the catalytic oxidation of tertiary and secondary amines, carbon catalysts prepared for use according to this invention improve the oxidative removal of carboxymethyl groups and phosphonomethyl groups from tertiary amines as well as the catalytic oxidation of N - (phosphonomethyl-imino)diacetic acid.

The present invention can be more clearly illustrated by the following examples.

Example 1

This example illustrates the improved results that are obtained by the catalysts prepared for use according to this invention in the conversion of a tertiary amine to a secondary amine.

Twenty-two powdered activated carbon samples were obtained from commercial sources, and a portion of each was subjected to the two-step treatment process described above. Approximately 12 grams of the carbon were placed in a 250 milliliter round-bottomed flask equipped with a magnetic stirrer. Then, 100 milliliters of 18.1 percent nitric acid was added to the flask and the contents were heated to about 85°C to about 100°C for six hours. The flask was allowed to cool to room temperature and the carbon was separated from the acid solution by filtration on a porous frit. The carbon was dried overnight in an oven at 85°C, then placed in a ceramic pyrolysis dish. The dish and the carbon were placed in a quartz tube. Dry nitrogen was passed through the tube while heating the tube and contents to approximately 930°C. Heating was continued for one hour. The heating was discontinued and the tube and contents were allowed to cool to room temperature while maintaining the flow of nitrogen over the carbon during cooling.

A portion of the treated and untreated carbon from each sample was then used as a catalyst in the oxidation of 7.3 gm N - (phosphonomethylimino)diacetic acid in 92 ml of water to produce N - phosphonomethylglycine. The catalyst charge was 1.2 gm for each run. Data obtained from observing each reaction are shown below in Table 1. The amin oxidation was performed in an autoclave made by

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Autoclave Engineers at 85°C and 50—55 psig oxygen pressure using an oxygen flow rate through the autoclave of 200 ml/min.

TABLE 1

Amine oxidation time (minutes)

Carbon type	Treated catalyst	Untreated catalyst
Calgon C	20	40
Calgon BL	17	38
Calgon RC	11	50
Darco GFP	15	36
Darco FM-1	10	66
Darco TRS	13	58
Darco S51	18	80
Darco S-51FF	10	55
Darco S-51K	13	113
Darco BG	13	40
Darco KB	14	136
Darco FM-1	11	66
Norit W20	16	69
Norit F	15	61
Norit FQA	23	>100
Norit SA4	11	39
Norit PN3	11	36
Norit A	8	46
Nuchar Aqua Pac	18	75
Nuchar Aqua S	10	57
Nuchar Experimental "A"	12	29
Nuchar Experimental "B"	10	85

Example 2

Six portions of Norit W20 carbon were subjected to the two-step treatment of Example 1 except that the pyrolysis time was varied from one to six hours. Results are shown in Table 2.

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TABLE 2

	Pyrolysis time (hours)	Amine oxidation time (minutes)	
		Treated catalyst	Untreated catalyst
5	1	16	69
10	2	11	—
	3	11	—
	4	11	—
15	5	6	—
	6	10	—

Example 3

In a 1.9 cm I.D. x 40.6 cm length quartz tube is placed 2.5 gm of Calgon C 450 activated carbon. The tube is connected to a gas stream resulting from sparging a 70 to 100 ml/min. N₂ stream through a 70°C, 10% NH₄OH aqueous solution. The quartz tube is then placed in a preheated 30.5 cm tubular furnace and pyrolyzed at 930°C for 60 min. and cooled to room temperature under a dry N₂ atmosphere without contacting any air.

The above carbon is used to oxidize various tertiary amines to secondary amines in a 300 ml autoclave made by "Autoclave Engineering" at 85°C, 3.44x10⁵ N/m² pressure and 200 ml/min. O₂ flow rate. The samples are analyzed by HPLC. The concentration of the reactant, catalyst load, and reaction times of treated catalyst vs. untreated catalyst of various tertiary amines are listed in Table 3 along with the reaction end point which can be determined by any one of several convenient methods known to those skilled in the art.

TABLE 3

	Reactant	Reactor-load	Amine oxidation time (minutes)		
			Untreated catalyst	Treated catalyst	Desired product
40	Nitrilotriacetic acid	4 gm Reactant 96 ml H ₂ O 0.2 gm Catalyst	>100	19.5	Iminodiacetic acid
45	N-phosphonomethyl-N-(n-propyl)glycine	2.0 gm Reactant 98 ml H ₂ O 0.1 gm Catalyst	>60	10	N-n-propyl-aminomethyl-phosphonic acid
50	N-phosphonomethylimino-diacetic acid	7.5 gm Reactant 92 ml H ₂ O 0.2 gm Catalyst	>400	33	N-phosphono-methylglycine
55	Trisphosphonomethylamine N(CH ₂ PO ₃ H ₂) ₃	5 gm Reactant 95 ml H ₂ O 0.2 gm Catalyst	>100	61.5	Bisphosphono-methylamine

Example 4

In a 1.9 cm I.D. x 35.6 cm long quartz tube was placed 3.55 gm of Norit W-20 activated carbon. The tube was connected to streams of 50 ml/min. of NH₃ gas and 89 ml/min. of steam and then placed in a preheated 30.5 cm tubular furnace and pyrolyzed at 930°C for 30 minutes. The tube was then cooled to room temperature under a dry N₂ atmosphere without any contact with air. The resulting carbon gave 54% weight loss.

Then, 7.3 gm of N - (phosphonomethylimino)diacetic acid, 1.2 gm of the above catalyst and 92 ml of H₂O were mixed in a 300 ml autoclave made by "Autoclave Engineering" and oxidized at 70°C, 3.44x10⁵ N/m²

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O₂ pressure and 200 ml/min. O₂ flow rate. The reaction finished at 9.7 min. The rate of reaction using the treated catalyst was 11.4 times faster than the reaction using the untreated catalyst.

Claims

1. A process for the selective production of secondary amines from tertiary amines and of primary amines from secondary amines by bringing together under reaction conditions a tertiary amine or a secondary amine, respectively, with oxygen or an oxygen-containing gas in the presence of an activated carbon catalyst, characterised in that the catalyst is an activated carbon catalyst wherein oxides have been removed from the surface thereof.
2. A process of Claim 1 wherein a secondary amine is produced from a tertiary amine.
3. A process of Claim 2 wherein the tertiary amine is a N-phosphonomethyl tertiary amine.
4. A process of Claim 3 wherein N-phosphonomethylglycine is produced from N-(phosphonomethylimino)diacetic acid.
5. A process according to any of Claims 1 to 4 wherein the activated carbon catalyst has been prepared by pyrolysing activated carbon at a temperature in the range of about 800°C to about 1200°C while simultaneously passing over the activated carbon a gas stream comprising an oxygen-containing gas and NH₃, the said gas stream containing not more than 90 parts by volume of the oxygen-containing gas per 100 parts by volume of gas stream.
6. The process of Claim 5 wherein the oxygen-containing gas is selected from H₂O, NO_x, O₂, CO₂, SO₂ and mixtures thereof.
7. The process of Claim 5 wherein the oxygen-containing gas is steam.
8. A process according to any of Claims 1 to 4 wherein the activated carbon catalyst has been prepared by subjecting activated carbon to an oxidizing agent, and thereafter pyrolysing the carbon in an oxygen-free atmosphere at a temperature in the range of 800°C to 1200°C.
9. A process of Claim 8 wherein the oxidizing agent is selected from liquid nitric acid, nitric acid vapours, nitrogen dioxide, CrO₃, air, oxygen, H₂O₂, and hypochlorite.
10. A process of Claim 9 wherein the carbon is pyrolyzed in an oxygen-free atmosphere containing ammonia.
11. A process of Claim 8 wherein the oxidizing agent is liquid nitric acid.

Patentansprüche

1. Verfahren zur selektiven Herstellung von sekundären Aminen aus tertiären Aminen und von primären Aminen aus sekundären Aminen durch Zusammenbringen eines tertiären Amins bzw. eines sekundären Amins mit Sauerstoff oder einem sauerstoffhaltigen Gas in Anwesenheit eines Aktivkohlekatalysators unter Reaktionsbedingungen, dadurch gekennzeichnet, daß der Katalysator ein Aktivkohlekatalysator ist, von dessen Oberfläche Oxide entfernt wurden.
2. Verfahren nach Anspruch 1, worin ein sekundäres Amin aus einem tertiären Amin hergestellt wird.
3. Verfahren nach Anspruch 2, worin das tertiäre Amin ein N-Phosphonomethyl-tert.amin ist.
4. Verfahren nach Anspruch 3, worin N - Phosphonomethylglycin aus N - (Phosphonomethylimino) - diessigsäure hergestellt wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, worin der Aktivkohlekatalysator hergestellt wurde durch Pyrolysieren von Aktivkohlenstoff bei einer Temperatur im Bereich von etwa 800 bis etwa 1200°C, wobei gleichzeitig über die Aktivkohle ein Gasstrom umfassend ein sauerstoffhaltiges Gas und NH₃ geleitet wird, wobei dieser Gasstrom nicht mehr als 90 Vol. Teile sauerstoffhaltiges Gas pro 100 Vol. Teile Gasstrom enthält.
6. Verfahren nach Anspruch 5, worin das sauerstoffhaltige Gas ausgewählt wird aus H₂O, NO_x, O₂, CO₂, SO₂ und Mischungen hiervon.
7. Verfahren nach Anspruch 5, worin das sauerstoffhaltige Gas Dampf ist.
8. Verfahren nach einem der Ansprüche 1 bis 4, worin der Aktivkohlekatalysator hergestellt wurde, indem Aktivkohle einem Oxidationsmittel ausgesetzt und danach die Kohle in einer sauerstofffreien Atmosphäre bei einer Temperatur im Bereich von 800 bis 1200°C pyrolysiert wird.
9. Verfahren nach Anspruch 8, worin das Oxidationsmittel ausgewählt wird aus flüssiger Salpetersäure, Salpetersäuredämpfen, Stickstoffdioxid, CrO₃, Luft, Sauerstoff, H₂O₂ und Hypochlorit.
10. Verfahren nach Anspruch 9, worin die Kohle in einer ammoniakhaltigen sauerstofffreien Atmosphäre pyrolysiert wird.
11. Verfahren nach Anspruch 8, worin das Oxidationsmittel flüssige Salpetersäure ist.

R vëndications

1. Procédé pour la préparation sélective d'amines secondaires à partir d'amines tertiaires et d'amines primaires à partir d'amines secondaires en mettant en contact dans des conditions de réaction une amine tertiaire ou une amine secondaire, respectivement, avec de l'oxygène ou un gaz oxygéné en présence d'un

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catalyseur de carbone activé, caractérisé en ce que le catalyseur est un catalyseur de carbone activé de la surface duquel les oxydes ont été éliminés.

2. Procédé selon la revendication 1, dans lequel une amine secondaire est préparée à partir d'une amine tertiaire.

5 3. Procédé selon la revendication 2, dans lequel l'amin tertiaire est une N - phosphonométhyl amine tertiaire.

4. Procédé selon la revendication 3, dans lequel la N - phosphonométhylglycine est préparée à partir de l'acide N - (phosphonométhylimino)diacétique.

10 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le catalyseur de carbone activé a été préparé en pyrolysant du carbone activé à une température dans l'intervalle d'environ 800°C à environ 1200°C tout en faisant passer simultanément sur le carbone activé un courant gazeux comprenant un gaz oxygéné et du NH_3 , ce courant gazeux ne contenant pas plus de 90 parties en volume du gaz oxygéné pour 100 parties en volume du courant gazeux.

15 6. Procédé selon la revendication 5, dans lequel le gaz oxygéné est choisi parmi H_2O , NO_x , O_2 , CO_2 , SO_2 et des mélangés de ceux-ci.

7. Procédé selon la revendication 5, dans lequel le gaz oxygéné est de la vapeur.

8. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le catalyseur de carbone activé a été préparé en soumettant du carbone activé à un agent oxydant, puis en pyrolysant le carbone dans une atmosphère exempte d'oxygène, à une température dans l'intervalle de 800 à 1200°C.

20 9. Procédé selon la revendication 8, dans lequel l'agent oxydant est choisi parmi l'acide nitrique liquide, les vapeurs d'acide nitrique, le bioxyde d'azote, CrO_3 , l'air, l'oxygène, H_2O_2 et l'hypochlorite.

10. Procédé selon la revendication 9, dans lequel le carbone est pyrolysé dans une atmosphère exempte d'oxygène contenant de l'ammoniac.

11. Procédé selon la revendication 8, dans lequel l'agent oxydant est l'acide nitrique liquide.

